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<p>(21) International Application Number: PCT/US93/01626 (22) International Filing Date: 26 February 1993 (26.02.93) (30) Priority data: 858,150 27 March 1992 (27.03.92) US (60) Parent Application or Grant (63) Related by Continuation US 858,150 (CIP) Filed on 27 March 1992 (27.03.92) (71) Applicant (for all designated States except US): THE UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL [US/US]; 300 Bynum Hall, Campus Box 4100, Chapel hill, NC 27599-4100 (US).</p>		<p>(72) Inventor; and (75) Inventor/Applicant (for US only) : DeSIMONE, Joseph, M. [US/US]; 2002 Pathway Drive, Chapel Hill, NC 27516 (US). (74) Agents: SIBLEY, Kenneth, D. et al.; Bell, Seltzer, Park & Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published With international search report. With amended claims.</p>

(54) Title: METHOD OF MAKING FLUOROPOLYMERS

(57) Abstract

A process for making a fluoropolymer is disclosed. The process comprises solubilizing a fluoromonomer in solvent comprising a carbon dioxide fluid, and then polymerizing the fluoromonomer to produce the fluoropolymer. A preferred solvent for carrying out the process is supercritical carbon dioxide; preferred fluoromonomers for carrying out the process are fluoroacrylate monomers such as 1,1-dihydroperfluorooctyl acrylate. The polymerization step is preferably carried out in the presence of an initiator such as azobisisobutyronitrile.

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METHOD OF MAKING FLUOROPOLYMERS

Cross Reference to Related Applications

This application is a continuation-in-part of copending U.S. Patent Application Serial No. 07/858,150, filed March 27, 1992.

5

Field of the Invention

The present invention relates to a method of making fluoropolymers, including copolymers thereof, in a solvent comprising a carbon dioxide fluid such as supercritical carbon dioxide.

10

Background of the Invention

Chlorofluorocarbons (CFCs) have been identified as one of the main causes of the depletion of atmospheric ozone. As a result, extensive effort has been directed towards discovering alternatives to CFCs in a variety of applications. In addition to the utilization of CFCs as refrigerants and aerosols, CFCs are commonly used as solvents for the manufacture of fluoropolymers, which are generally insoluble in traditional organic solvents but can often be solubilized in CFCs. Hence, there is a need for alternative methods of manufacturing fluoropolymers.

A supercritical fluid (SCF) is a substance above its critical temperature and critical pressure (or "critical point"). Compressing a gas normally causes a phase separation and the appearance of a
5 separate liquid phase. However, if the fluid is in a supercritical state, compression will only result in density increases: no liquid phase will be formed. The physical properties of supercritical fluids are highly unpredictable, and the use of supercritical fluids for
10 carrying out polymerization processes has received relatively little attention.

S. Kumar et al., *Polym. Prep.* 27, 224 (1986), describe the free radical precipitation polymerization of polystyrene chains in supercritical ethane. The
15 styrene monomers were dissolved in ethane and polymerized with azobisisobutyronitrile ("AIBN") as an initiator using an apparatus having a high-pressure optical cell.

V. Sarai and E. Kiran, *Polym. Prep.* 31, 687 (1990), describe the free radical polymerization of
20 styrene in supercritical ethane, propane, and butane, using AIBN, t-butyl peroxide and t-butyl peroxybenzoate as initiators.

K. Scholsky, *Polym. Prep.* 31, 685 (1990), describe a variety of polymerization reactions using
25 supercritical fluids. The article summarizes publications on the polymerization of fluorinated olefins, such as vinyl fluoride, tetrafluoroethylene, the copolymerization of tetrafluoroethylene and sulfur dioxide, and polyperfluoropropylene. Other fluorinated
30 olefins mentioned include n-tetradecafluoroheptene-1, n-perfluoropentadiene-1,4, vinylidene chlorofluoride, and a variety of vinylic monomers. The polymerization of fluoropolymers in carbon dioxide is not suggested.

35 E. Beckman and R. Smith, *J. Phys. Chem.* 94, 345 (1990) describe the microemulsion polymerization of acrylamide ($\text{CH}_2\text{CHCONH}_2$) in supercritical fluids, and

particularly the inverse microemulsion polymerization of water-soluble acrylamide monomers within near-critical and supercritical alkane continuous phases.

5 G.S. Varadarajan, *Free Radical Polymerization in Supercritical Fluid Solvents* (November 29, 1990) (MIT Doctoral Thesis) describes the free radical polymerization of polymethylmethacrylate (MMA) ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$) in supercritical carbon dioxide using AIBN as an initiator. The polymerization of
10 fluoromethacrylates in supercritical carbon dioxide is not suggested.

Canadian Patent No. 1,274,942 is directed to acrylic acid polymerization by homopolymerizing carboxylic acids such as acrylic acid and methacrylic
15 in supercritical carbon dioxide. The polymerization of fluoroacrylate or fluoromethacrylate monomers in supercritical carbon dioxide is not suggested.

V. Krukonis and M. McHugh, *Supercritical Fluid Extraction*, 156-158, describes the fractionation
20 of a perfluoroalkylpolyether oil and a chlorotrifluoroethylene oligomer in supercritical carbon dioxide, but does not suggest the polymerization of fluoromonomers in supercritical carbon dioxide.

Summary of the Invention

25 A process for making a fluoropolymer is disclosed. The process comprises solubilizing a fluoromonomer in a solvent, the solvent comprising carbon dioxide fluid; and then polymerizing the fluoromonomer in said solvent to produce said
30 fluoropolymer. The fluoromonomer may be a fluoroacrylate monomer, a fluorostyrene monomer, a fluorinated vinyl ether monomer, or a fluoroalkylene oxide oligomer. Fluoromonomers of the type which undergo free radical polymerization are preferred.
35 The polymerization reaction is, in general, carried out in the presence of an initiator. The carbon dioxide

fluid may be liquid carbon dioxide or supercritical carbon dioxide.

In one embodiment of the foregoing, the process may further comprise solubilizing a comonomer in the carbon dioxide fluid, with the polymerizing step comprises copolymerizing the fluoromonomer with the comonomer.

The fluoropolymers can be used as a composition for altering surface tension properties, e.g., to create low energy surfaces such as for stain resistance properties.

Brief Description of the Drawings

In the drawings which form a part of the disclosure of the invention:

Figure 1 is a phase equilibria diagram of poly(chlorotrifluoroethylene) in carbon dioxide at 40°C, wherein the x axis of the diagram represents the weight fraction of the sample, and the y axis represents pressure in bars; and

Figure 2 is a phase equilibria diagram of poly(1,1-dihydroperfluorooctyl acrylate) in carbon dioxide at 60°C, wherein the x axis of the diagram represents the weight fraction of the sample, and the y axis represents pressure in bars.

Detailed Description of the Invention

The term "fluoropolymer," as used herein, has its conventional meaning in the art. See generally *Fluoropolymers* (L. Wall, Ed. 1972) (Wiley-Interscience Division of John Wiley & Sons); see also *Fluorine-Containing Polymers*, 7 Encyclopedia of Polymer Science and Engineering 256 (H. Mark et al. Eds., 2d Ed. 1985). Likewise, the term "fluoromonomer" refers to fluorinated precursor monomers employed in the synthesis of fluoropolymers. The term "solubilizing," as used herein, is used to indicate that the

fluoromonomers are in the same phase as the carbon dioxide fluid in the process of the present invention; hence the polymerization reactions of the present invention are solution polymerizations, as opposed to heterogeneous polymerizations or bulk polymerizations, with these terms having their ordinary meaning in the industry. See, e.g., G. Odian, *Principles of Polymerization*, 301-334 (3d Ed. 1991) (Wiley Interscience).

Any suitable fluoromonomer may be used, including, but not limited to, fluoroacrylate monomers, fluoroolefin monomers, fluorostyrene monomers, fluoroalkylene oxide monomers (e.g., perfluoropropylene oxide, perfluorocyclohexene oxide), fluorinated vinyl alkyl ether monomers, and the copolymers thereof with suitable comonomers, wherein the comonomers are fluorinated or unfluorinated. Fluoromonomers which are polymerized by a free radical polymerization process are preferred.

Fluorostyrenes and fluorinated vinyl alkyl ether monomers which may be polymerized by the method of the present invention include, but are not limited to, α -fluorostyrene; β -fluorostyrene; α,β -difluorostyrene; β,β -difluorostyrene; α,β,β -trifluorostyrene; α -trifluoromethylstyrene; 2,4,6-Tris(trifluoromethyl)styrene; 2,3,4,5,6-pentafluorostyrene; 2,3,4,5,6-pentafluoro- α -methylstyrene; and 2,3,4,5,6-pentafluoro- β -methylstyrene. These monomers are particularly useful as comonomers in the method of the present invention.

Tetrafluoroethylene copolymers which are amorphous or have low melting points can be prepared by the method of the present invention and include, but are not limited to, tetrafluoroethylene-hexafluoropropylene copolymers, tetrafluoroethylene-perfluorovinyl ether copolymers (e.g., copolymers of tetrafluoroethylene with perfluoropropyl vinyl ether),

tetrafluoroethylene-ethylene copolymers, and perfluorinated ionomers (e.g., perfluorosulfonate ionomers; perfluorocarboxylate ionomers).

Fluorocarbon elastomers (see, e.g., 7 Encyclopedia of Polymer Science & Engineering 257) are a group of amorphous fluoroolefin polymers which can be produced by the process of the present invention and include, but are not limited to, poly(vinylidene fluoride-co-hexafluoropropylene); poly(vinylidene fluoride-co-hexafluoropropylene-co-tetrafluoroethylene); poly[vinylidene fluoride-co-tetrafluoroethylene-co-perfluoro(methyl vinyl ether)]; poly[tetrafluoroethylene-co-perfluoro(methyl vinyl ether)]; poly(tetrafluoroethylene-co-propylene; and poly(vinylidene fluoride-co-chlorotrifluoroethylene).

The term "fluoroacrylate monomer," as used herein, refers to esters of acrylic acid ($H_2C=CHCOOH$) or methacrylic acid ($H_2C=CCH_3COOH$), where the esterifying group is a fluorinated group such as perfluoroalkyl. A specific group of fluoroacrylate monomers useful in the method of the invention are compounds represented by formula (I):



wherein:

n is 1 or 2;
 R^1 is hydrogen or methyl; and
 R^2 is a perfluorinated aliphatic or perfluorinated aromatic group, such as a perfluorinated linear or branched, saturated or unsaturated C1 to C10 alkyl, phenyl, or naphthyl.

In a particular embodiment of the invention, R^2 is a C1 to C8 perfluoroalkyl or $-CH_2NR^3SO_2R^4$, wherein R^3 is C1-C2 alkyl and R^4 is C1 to C8 perfluoroalkyl.

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The term "perfluorinated," as used here in, means that all or essentially all hydrogen atoms on an organic group are replaced with fluorine.

Monomers illustrative of Formula (I) above, and their abbreviations as used herein, include the following:

2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate ("EtFOSEA");

2-(N-ethylperfluorooctanesulfonamido) ethyl methacrylate ("EtFOSEMA");

2-(N-methylperfluorooctanesulfonamido) ethyl acrylate ("MeFOSEA");

2-(N-methylperfluorooctanesulfonamido) ethyl methacrylate ("MeFOSEMA");

1,1-Dihydroperfluorooctyl acrylate ("FOA"); and

1,1-Dihydroperfluorooctyl methacrylate ("FOMA").

In the process of the invention, the fluoroacrylate monomers may be polymerized in the presence of a free radical polymerization initiator. Any of the various organic and inorganic initiators which are known for the polymerization of monomers can be used, so long as it is compatible with carbon dioxide. The polymerization is carried out at two different temperatures by first subjecting the monomers to initial polymerization at a lower temperature, and then completing the polymerization at a substantially higher temperature.

Organic free radical initiators are preferred and include, but are not limited to, the following: acetylcyclohexanesulfonyl peroxide; diacetyl peroxydicarbonate; dicyclohexyl peroxydicarbonate; di-2-ethylhexyl peroxydicarbonate; tert-butyl perneodecanoate; 2,2'-azobis(methoxy-2,4-dimethylvaleronitrile); tert-butyl perpivalate; dilauroyl peroxide; dilauroyl peroxide; 2,2'-

azobis(2,4-dimethylvaler nitrile); tert-butylazo-2-cyanobutane; dibenzoyl peroxide; tert-butyl per-2-ethylhexanoate; tert-butyl permaleate; 2,2-azobis(isobutyronitrile); bis(tert-butylperoxy)cyclohexane; tert-butyl peroxyisopropylcarbonate; tert-butyl peracetate; 2,2-bis(tert-butylperoxy)butane; dicumyl peroxide; ditert-amyl peroxide; di-tert-butyl peroxide; p-menthane hydroperoxide; pinane hydroperoxide; cumene hydroperoxide; and tert-butyl hydroperoxide. Preferably, the initiator is azobisisobutyronitrile ("AIBN").

The process of the invention is carried out in a carbon dioxide fluid, e.g., carbon dioxide in a liquid or supercritical state. As will be appreciated by those skilled in the art, all gases have a critical temperature above which the gas cannot be liquified by increasing pressure, and a critical pressure or pressure which is necessary to liquify the gas at the critical temperature. For example, carbon dioxide in its supercritical state exists as a form of matter in which its liquid and gaseous states are indistinguishable from one another. For carbon dioxide, the critical temperature is about 31°C (88°F) and the critical pressure is about 73 atmospheres or about 1070 psi. The term "supercritical carbon dioxide" as used herein refers to carbon dioxide at a temperature greater than about 31°C and a pressure of greater than about 1070 psi.

Liquid carbon dioxide may be obtained at temperatures of from about -15°C to about -55°C and pressures of from about 77 psi to about 335 psi.

One or more solvents and blends thereof may optionally be included in the carbon dioxide. Illustrative solvents include, but are not limited to, tetrahydrofuran, cyclohexane, and methanol. Such

solvents are typically included in an amount, by weight, of up to about 20%.

The polymerization initiators are used in the amounts conventionally employed for polymerization.

5 For example, the initiator may be used in an amount of about 0.01 to 10, preferably about 0.01 to 5, parts by weight per 100 parts by weight monomer.

The polymerization reaction may be carried out at a temperature of about -55°C to about 300°C, and
10 is typically carried out at a temperature of about -30 to 100°C. The reaction may be carried out at a pressure ranging from about 15 psi to about 45000 psi, and is typically at a pressure of from about 500 psi to about 10000 psi.

15 In alternative embodiments of the present invention, at least one monomer or comonomer is solubilized in carbon dioxide and copolymerized with the fluoromonomer. Any suitable monomers or comonomers can be employed, including, but not limited to,
20 acrylate, methacrylate, acrylamide, methacrylamide, styrenics, ethylene, and vinyl ether monomers. The copolymerizations of the present invention may be carried out under temperature and pressure conditions similar to those given above.

25 The polymerization can be carried out batchwise or continuously with thorough mixing of the reactants in any appropriately designed high pressure reaction vessel (i.e., capable of withstanding pressures up to 45000 psi). To remove the heat evolved
30 during the polymerization, advantageously the pressure apparatus includes a cooling system. Additional features of the pressure apparatus used in accordance with the invention include heating means such as an electric heating furnace to heat the reaction mixture
35 to the desired temperature and mixing means, i.e., stirrers such as paddle stirrers, impeller stirrers, or

multistage impulse countercurrent agitators, blades, and the like.

The polymerization can be carried out, for example, by placing the monomer and initiator in the pressure apparatus and introducing carbon dioxide in liquid form. The reaction vessel is closed and the reaction mixture brought to the polymerization temperature and pressure. Alternatively, only a part of the reaction mixture may be introduced into an autoclave and heated to the polymerization temperature and pressure, with additional reaction mixture being pumped in at a rate corresponding to the rate of polymerization. In another possible procedure, some of the monomers are initially taken into the autoclave in the total amount of carbon dioxide and the monomers or comonomers are pumped into the autoclave together with the initiator at the rate at which the polymerization proceeds.

When the polymerization is complete the reaction mixture is cooled (if necessary), the carbon dioxide separated off (e.g., by simply venting to the atmosphere), and the polymer collected. After separation of the carbon dioxide, the polymer can be collected simply by physical isolation, or by dissolution and precipitation, for example, by adding Freon-113[™] or α,α,α -trifluorotoluene to the polymer to dissolve the polymer and recover it from the reaction vessel and then precipitating the same with methanol.

The following Examples are provided to further illustrate the present invention. In the Examples, SCF means supercritical fluid; AIBN means azobisisobutyronitrile; MMA means polymethylmethacrylate; psi means pounds per square inch; g means grams; mg means milligrams; mL means milliliters; min means minutes; Mw means weight average molecular weight; Mn means number average molecular weight; MWD means molecular weight distribution (Mw/Mn); mmol means

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millimoles; dL/g means deciliters per gram; cm means centimeters; THF means tetrahydrofuran; DMF means N,N-dimethylformamide; DMAc means N,N-dimethylacetamide; [n] means intrinsic viscosity; NMR means nuclear magnetic resonance; GPC means gel permeation chromatography; FTIR means fourier transform infrared; IR means infrared; and temperatures are given in degrees celsius. These examples are illustrative of the invention, and should not be construed as limiting thereof.

EXAMPLES 1-17

Solubility, Polymerization and Copolymerization of Fluoroacrylate Monomers

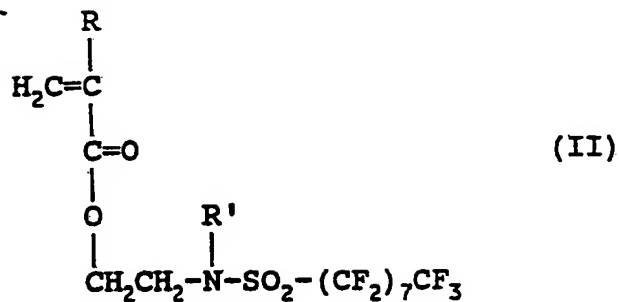
EXAMPLE 1

Experimental Procedures

Materials. Five fluoromonomers, illustrated by Formula (II) and Table 1 and Formula (III) and Table 2, were kindly provided by Minnesota Mining and Manufacturing Company (3M). MeFOSEA, EtFOSEA and EtFOSEMA were purified by recrystallization in methanol. 1,1-Dihydroperfluorooctyl acrylate (FOA) was purified by running through Al_2O_3 column to remove the inhibitor. AIBN (Kodak) was recrystallized twice from methanol. Carbon dioxide (Matheson, 99.99%) was passed through copper oxide catalyst column to remove trace amounts of oxygen and then through a molecular sieve(3A) column to remove trace amounts of moisture. Freon-113 ($CF_2ClCFCl_2$) was fractionally distilled before use. Methanol (Mallinckrodt) was used as received.

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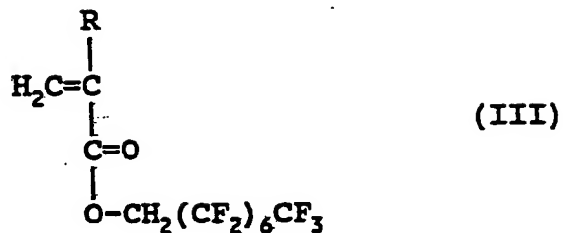
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Table 1.
Fluorinated Monomers of Formula (II)

<u>Name</u>	<u>R</u>	<u>R'</u>
MeFOSEA	H	CH ₃
EtFOSEA	H	CH ₂ CH ₃
MeFOSEMA	CH ₃	CH ₃
EtFOSEMA	CH ₃	CH ₂ CH ₃

15

20



25

Table 2.
Fluorinated Monomers of Formula (III)

<u>Name</u>	<u>R</u>
FOA	H
FOMA	CH ₃

EXAMPLE 2

Comparative Example: Polymerization in Freon 113

Before running polymerizations in supercritical carbon dioxide, a series of poly(perfluoroalkyl acrylate)s and poly(perfluoroalkyl methacrylate)s were prepared using free radical polymerization methods in Freon-113 and in α,α,α -trifluorotoluene and studied their solubility in both liquid and supercritical carbon dioxide. The fluoromonomers employed for this study are those set forth in Tables 1 and 2 above. The polymerization conditions (feed ratios of monomers, initiator and solvents), intrinsic viscosities and molecular weight data are summarized at Table 3.

A typical procedure is described below. EtFOSEA (5 g), azobisisobutyronitrile (AIBN) (10 mg) and 10 mL of Freon-113 were put into a 50 mL test tube. After sealing the tube with a rubber septum, the solution was purged with argon for ca. 15 min, placed in a water bath at 60°C and left to polymerize for ca. 20 hours. The tube was opened next day and ca. 30 mL of Freon-113 was added to dilute the polymer solution, followed by precipitation of polymer into methanol. The polymer was filtered and dried in vacuum oven overnight. All of the monomers were polymerized in Freon-113 at 60°C except MeFOSEA which was polymerized in α,α,α -trifluorotoluene at 70°C due to solubility considerations.

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Table 3

	Sample	Feed Ratio			[n]	Mw	Mn	MWD
		monomer (g)	AIBN (mg)	solvent (ml)				
5	P(EtFOSEA)							
	910607-1	2	5	10	0.14	7.68e4	1.13e4	6.79
	910607-2	2	10	10	0.11	9.23e4	1.32e4	7.02
	910607-3	2	20	10	0.078	7.67e4	2.06e4	3.73
	910614-0	3	2+2	2	0.44	1.24e5	5.14e4	2.41
	910614-1	5	5	10	0.28	1.14e5	1.39e4	8.20
10	910614-2	5	10	10	0.28	1.56e5	5.56e4	2.80
	910614-3	5	20	10	0.24	1.38e5	5.46e4	2.54
	P(EtFOSEMA)							
	910710-3	5	5	10	0.13	7.20e4	8.23e3	8.75
15	P(FOA)							
	910710-1	5	5	10	0.21	1.10e6	2.90e5	3.78
	P(FOMA)							
	910710-2	5	5	10	gel-like			
	910711	5	5	20	0.26*	unable to filter		
20	P(MeFOSEA)**							
	910620-1	5	10	20	0.077			
	910620-2	5	20	20	0.066			
	910620-3	5	30	20	0.010			

All polymerizations are run at 60°C.

* The viscosity of the soluble part.

**Polymerized in , , -trifluorot luene.

EXAMPLE 3

Solubility Evaluation in Carbon Dioxide

The solubilities of poly(EtFOSEA) and poly(MeFOSEA) in carbon dioxide were measured using a flow system, the results of which are set forth at Table 4. Poly(EtFOSEA) was found to be very soluble in both liquid and supercritical carbon dioxide (about 25 wt.%). Poly(MeFOSEA) dissolved in liquid CO₂ at 3000 psi at room temperature. A view cell study discussed below verified that the polymer was also soluble in supercritical CO₂.

For comparison, the solubility of poly(methyl methacrylate) (PMMA) in both liquid and supercritical CO₂ was also studied. Quite differently, PMMA of even lower molecular weight than the two fluoropolymers discussed above is insoluble in carbon dioxide with the pressure ranging from 2000 to 5000 psi and temperature ranging from room temperature to 160°C.

To ensure that the fluoropolymers form homogeneous solutions with carbon dioxide, the solubility of the five fluoropolymers was also determined using a view cell. The results of the observations are set forth at Table 5. We observed that all the polymers dissolved and formed clear solutions in carbon dioxide at moderate pressures. Comparatively, poly(FOA) and poly(FOMA) are easier to dissolve in carbon dioxide than poly-(EtFOSEMA), poly(EtFOSEA) and poly(MeFOSEA), but all of the polymers dissolve.

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Table 4

Solubility study of F-polymers by flow system:

	Sampl	[n]	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	T(°C)	P(psi)	Solubility (wt.%)
5	P(EtFOSEA)	0.44	1.24	5.14	29	5000	25
	P(EtFOSEA)	0.28	1.14	1.39	60	4000	25
	P(MeFOSEA)	0.077	—	—	25	3000	15-20
	PMMA	—	0.22	1.93	29-160	2000-5000	0

Table 5

Solubility study of F-polymers by view cell:

	Sample	[n]	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	T(°C)	P(psi)	Conc. wt.%vol
10	P(EtFOSEA)	0.44	1.24	5.14	25	7000	9
	P(EtFOSEA)	0.24	1.38	5.46	25	3000	5
	P(MeFOSEA)	0.077	—	—	60	3700	5
	P(FOA)	0.21	11.0	29.0	25	2000	5
15	P(FOA)	0.21	11.0	29.0	25	3000	10
	P(FOMA)	0.26	—	—	25	2000	5
	P(EtFOSEMA)	0.13	0.72	0.82	25	4000	5

* Pressure at which the polymer totally dissolve.

EXAMPLE 4

20 Polymerization of 1,1-dihydroperfluorooctyl
 Acrylate (FOA) in Carbon Dioxide

FOA (5.0 g, 11.0 mmol, purified by running
 thr ough Al₂O₃ column) and AIBN (50 mg, 0.30 mmol,
 recrystallized twice from methanol) were put into a 10
 25 mL high pressure r action cell with a micromagnetic
 stir bar inside. The reaction cell was purged with

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argon for ca. 10 minutes and then filled with carbon dioxide to a pressure of less than 1000 psi. Over a period of one hour, the cell was heated to 60°C and the pressure was increased to 3000 psi by the addition of more CO₂. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear.

At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved with Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.25 g of transparent viscous polymer (yield: 65%).

Characterizations: ¹H NMR spectrum showed the expected pattern, without vinyl proton peaks of the monomer and without any indication of incorporation of carbon dioxide onto the polymer backbone. The intrinsic viscosity was measured to be 0.19 dL/g in Freon-113 at 30°C. The FTIR spectrum was consistent with the corresponding homopolymer made in Freon-113, with only one carbonyl peak at 1758 cm⁻¹.

EXAMPLE 5

Polymerization of FOA in carbon dioxide

FOA (2.0 g, 4.4 mmol) and AIBN (30 mg, 0.18 mmol) were put into the high pressure cell. Following the same procedure as described in Example 4, polymerization was proceeded at 3000 psi and 60°C for 24 hours, and 0.41 g of polymer was obtained (yield: 21%).

Characterizations: ¹H NMR and FTIR spectra were consist nt with those of the homopolymer made in Freon-113.

EXAMPLE 6

Polymerization of 1,1-dihydroperfluorooctyl
Methacrylate (FOMA) in Carbon Dioxide

FOMA (3.0 g, 6.41 mmol, purified by running
5 through Al_2O_3 column) and AIBN (30 mg, 0.18 mmol) were
put into the 10 mL high pressure reaction cell. The
reaction cell was purged with argon for ca. 10 minutes
then filled with carbon dioxide to a pressure of less
than 1000 psi. Over a period of one hour, the cell was
10 heated to 60°C, and the pressure was increased to 4000
psi by the addition of more CO_2 . The polymerization was
continued at these conditions for 48 hours, during
which the system was homogeneous and clear. At the end
of the polymerization, carbon dioxide was vented slowly
15 to leave the polymer in the cell. The polymer was
dissolved with Freon-113 and was precipitated into a
large excess of methanol. The polymer was isolated by
suction filtration, washed several times with methanol,
and dried in vacuo overnight to give 2.19 g of a white
20 powder (yield: 73%).

Characterizations: ^1H NMR and FTIR spectra
were consistent with those of the same polymer made in
Freon-113. The intrinsic viscosity was measured to be
0.06 dL/g in Freon-113 at 30°C.

25

EXAMPLE 7

Polymerization of FOMA in CO_2

FOMA (5.0 g, 10.7 mmol) and AIBN (50 mg, 0.3
mmol) was put into the 10 mL high pressure cell.
Following the same procedure described in Example 4,
30 the polymerization was carried out in CO_2 at 60°C and
5000 psi for 48 hours. During the entire course of the
polymerization, the solution was homogeneous and clear.
The polymer was isolated according to the same
procedure as described above.

35

Characterizations: ^1H NMR and FTIR spectra
were consistent with those of the same polymer made in

-19-

Fr on-113. The intrinsic viscosity was measured to be 0.06 dL/g in Freon-113 at 30°C.

EXAMPLE 8

5 Polymerization of 2-(N-methylperfluorooctane-sulfonamido) ethyl Acrylate (MeFOSEA) in Carbon Dioxide

MeFOSEA (5.0 g, 8.75 mmol, purified by recrystallization from methanol) and AIBN (50 mg, 0.30 mmol) were put into the 10 mL high pressure reaction cell. The reaction cell was purged with argon for ca. 10 minutes then filled with carbon dioxide to a pressure of less than 1000 psi. Over a period of one hour the cell was heated to 60°C and the pressure was increased to 5000 psi by the addition of more CO₂. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved in α,α,α -trifluorotoluene and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.2 g of white powder (yield: 64%).

25 Characterizations: FTIR spectra were consistent with those of the same polymer made in Freon-113.

EXAMPLE 9

Polymerization of MeFOSEA in Carbon Dioxide

30 MeFOSEA (1.0 g, 1.75 mmol) and AIBN (10 mg, 0.06 mmol) were put into the high pressure cell. Following the same procedure of Example 4, the polymerization was proceeded under 4000 psi and 60°C for 8 hours, and 0.19 g of polymer was obtained (yield: 19%).

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Characterizations: FTIR spectrum were consistent with the same polymer made in Freon-113. The intrinsic viscosity was measured to be 0.064 in α, α, α -trifluorotoluene at 70°C.

5

EXAMPLE 10

Polymerization of 2-(N-ethylperfluorooctane-sulfonamido) Ethyl Acrylate (EtFOSEA) in Carbon Dioxide

EtFOSEA (5.0 g, 8.53 mmol, purified by recrystallization from methanol) and AIBN (50 mg, 0.30 mmol) were put into the 10 mL high pressure view cell. The reaction cell was purged with argon for ca. 10 minutes then filled with carbon dioxide to a pressure of less than 1000 psi. Over a period of one hour the cell was heated to 60°C and the pressure was increased to 5000 psi by the addition of more CO₂. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved in Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.9 g of a white powder (yield: 78%).

25

Characterizations: ¹H NMR and FTIR spectra were consistent with those of the same polymer made in Freon-113. The intrinsic viscosity was measured to be 0.20 dL/g in Freon-113 at 30°C. Both the polymers made in CO₂ and in Freon-113 were purified by dissolving in Freon-113 and reprecipitating into methanol and an elemental analysis by ORS was performed. The results are summarized in Table 6 below.

30

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Table 6

Elemental Analysis of Poly(EtFOSEA) Made in
Carbon Dioxid and in Freon-113

5	Sample	% C	% H	% N	% F	% S
	P-Freon	28.69	1.86	2.21	51.47	5.05
	P-CO ₂	28.80	1.91	2.24	50.78	4.81
	Calculated	29.01	2.01	2.33	50.64	5.34
10						

EXAMPLE 11

Polymerization of 2-(N-ethylperfluorooctane-
sulfonamido) Ethyl Methacrylate (EtFOSEMA) in CO₂

EtFOSEMA (5.0 g, 8.33 mmol, purified by
15 recrystallization from methanol) and AIBN (50 mg, 0.30
mmol) were put into the same reaction vessel. The
reaction vessel was purged with argon for ca. 10
minutes then filled with carbon dioxide to a pressure
of less than 1000 psi. Over a period of one hour the
20 cell was heated to 60°C, and the pressure was increased
to 5000 psi by the addition of more CO₂. The
polymerization was continued at these conditions for 48
hours, during which the system was homogeneous and
clear. At the end of the polymerization, carbon
25 dioxide was vented slowly to leave the polymer in the
vessel. The polymer was dissolved in Freon-113 and
was precipitated into a large excess of methanol. The
polymer was isolated by suction filtration, washed
several times with methanol, and dried in vacuo
30 overnight to give 3.2 g of white powder.

Characterizations: ¹H NMR and FTIR spectra
w r consistent with thos of the same polymer made in
Freon-113. The intrinsic viscosity was measured to b
0.10 dL/g in Freon-113 at 30°C.

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EXAMPLE 12

Copolymerization of FOA with
Methyl Methacrylate (MMA) in CO₂

FOA (4.0 g, mmol, purified by running
5 through Al₂O₃ column), MMA (1.0 g, 10.0 mmol, purified
by vacuum distillation over CaH₂) and AIBN (50 mg, 0.30
mmol) were put into the 10 mL high pressure view cell.
The reaction cell was purged with argon for ca. 10
minutes then filled with carbon dioxide to less than
10 1000 psi. Over a period of one hour the cell was
heated to 60°C and the pressure was increased to 5000
psi by the addition of more CO₂. The polymerization was
continued at these conditions for 48 hours, during
which the system was homogeneous and clear. At the end
15 of the polymerization, carbon dioxide was vented slowly
to leave the polymer in the cell. The polymer was
dissolved in Freon-113 and was precipitated into a
large excess of methanol. The polymer was isolated by
suction filtration, washed several times with methanol,
20 and dried in vacuo overnight to give 3.25 g of
copolymer (yield: 65%). The copolymer was extracted
with THF three times to remove any possible PMMA
homopolymer.

Characterizations: Solubility of the
25 copolymer in normal solvents and Freon-113 was checked
and the results are summarized in Table 7 below.

Table 7

Solubility Test of PFOA-co-PMMA-1

	Solvent	solubility
5	Freon-113	soluble, but slightly cloudy
	acetone	liquified but insoluble
	THF	liquified but insoluble
	CH ₂ Cl ₂	swelled
10	toluene	swelled
	DMF	slightly swelled
	DMAc	slightly swelled

15 ¹H NMR and FTIR spectra were indicative of a statistical or random copolymer. Composition of the copolymer was calculated to be 58 mol% FOA from the ¹H NMR spectrum. IR spectrum showed two carbonyl peaks at 1758 (carbonyl of FOA segments) and 1734 cm⁻¹ (carbonyl of MMA segments), respectively. The intrinsic

20 viscosity was measured to be 0.10 dL/g in Freon-113 at 30°C.

EXAMPLE 13

Copolymerization of FOA and MMA in Carbon Dioxide

25 FOA (3.0 g, 6.6 mmol, purified by running through Al₂O₃ column), MMA (2.0 g, 20.0 mmol, purified by vacuum distillation over CaH₂) and AIBN (50 mg, 0.30 mmol) were put into the high pressure cell. The reaction cell was purged with argon for ca. 10 minutes then filled with carbon dioxide to less than 1000 psi.

30 Over a period of one hour the cell was heated to 60°C and the pressure was increased to 5000 psi by the addition of more CO₂. The polymerization system became nonhomogeneous after ca. 12 hours. After 48 hours, there existed two layers, with the bottom layer

35 accounting for ca. 1/4 of the total reactor volume and a cloudy upper layer accounting for ca. 3/4 of the

total volume. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved in Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.3 g of copolymer (yield: 66%). The copolymer was extracted with DMF three times.

Characterizations: ^1H NMR and FTIR spectra show the expected patterns. Composition of copolymer was calculated from proton NMR spectrum to be 27 mol% in FOA. Two carbonyl peaks appear on the IR spectrum (1758 and 1734 cm^{-1}). The intrinsic viscosity was measured to be 0.12 dL/g in acetone at 30°C. The solubilities of the copolymer in normal solvents are summarized in Table 8 below.

Table 8

Solubility of PFOA-co-PMMA-2 in Different Solvents

20	Solvent	Solubility
	Freon-113	soluble
	acetone	soluble
	THF	soluble
25	CHCl_3	soluble
	CH_2Cl_2	soluble (40 °C)
	toluene	soluble (100 °C)
	DMF	insoluble
	DMAc	insoluble

30

Since this copolymer is soluble in normal solvents, ^{13}C NMR and ^{19}F NMR spectra was measured in d_6 -acetone. Only two carbonyl peaks appeared on the spectrum (177, 178 ppm). The ^{19}F NMR spectrum showed six resonances. GPC was run with THF as solvent and polystyrene as standard. The results were $M_n = 5.10 \times 10^4$, $M_w = 7.45 \times 10^4$, $MWD = 1.46$.

35

EXAMPLE 14

Copolymerization of FOA and MMA
in CO₂ with THF as a Co-Solvent

FOA (3.0 g, 6.6 mmol), MMA (2.0 g, 20 mmol)
5 and AIBN (50 mg, 0.30 mmol) were put into the high
pressure cell. 1.0 mL (10 vol%) THF was added into the
mixture. The reaction cell was purged with argon for
ca. 10 minutes and then filled with carbon dioxide to
10 less than 1000 psi. Over a period of one hour the cell
was heated to 60°C, and the pressure was increased to
5000 psi by the addition of more CO₂. The
polymerization was continued at these conditions for 48
hours. The system was homogeneous for at least 30
hours at which time it became cloudy. The solution
15 remained homogenous for a longer time than the
polymerization reaction conducted without the cosolvent
(Example 13). At the end of the polymerization, carbon
dioxide was vented slowly to leave the polymer in the
cell. The polymer was dissolved in Freon-113 and was
20 precipitated into a large excess of methanol. The
polymer was isolated by suction filtration, washed
several times with methanol, and dried in vacuo
overnight to give 3.9 g of white polymer (yield: 78%).

Characterizations: GPC was run with THF as
25 solvent. The results were: $M_n = 5.50 \times 10^4$, $M_w =$
 8.23×10^4 , MWD = 1.50.

EXAMPLE 15

Copolymerization of FOA and n-butyl
Acrylate (BA) in Carbon Dioxide

30 FOA (4.0 g, 6.6 mmol), BA (1.0 g, 7.8 mmol,
purified by running through Al₂O₃ column) and AIBN (50
mg, 0.30 mmol) were put into the high pressure reaction
cell. The reaction cell was purged with argon for ca.
10 minutes then filled with carbon dioxide to less than
35 1000 psi. Over a period of one hour the cell was

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heated to 60°C and the pressure was increased to 5000 psi by the addition of more CO₂. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved with Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give a transparent elastic material which was purified by extracting with acetone overnight.

Characterizations: ¹H NMR and FTIR spectra were indicative of a random or statistical copolymer. Composition of the copolymer was calculated to be 59% FOA based on ¹H NMR. Two carbonyl resonances appeared in the IR spectrum (1760 and 1720 cm⁻¹). The intrinsic viscosity was 0.45 dL/g in Freon-113 at 30°C. The solubility of the copolymer is summarized in Table 9.

20

Table 9

The Solubility of PFOA-co-PBA in Different Solvents

Solvent		Solubility
25	Freon-113	soluble
	acetone	insoluble
	THF	insoluble
	CHCl ₃	dispersed but insoluble
	toluene	insoluble
30	DMF	insoluble

EXAMPLE 16

Copolymerization of FOA with Styrene in CO₂

FOA (4.0 g, 6.6 mmol), styrene (1.0 g, 9.6 mmol, purified by vacuum distillation) and AIBN (50 mg,

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0.30 mmol) were put into the high pressure reaction cell. The reaction cell was purged with argon for ca. 10 minutes then filled with carbon dioxide to less than 1000 psi. Over a period of one hour the cell was
5 heated to 60°C and the pressure was increased to 5000 psi by the addition of more CO₂. The polymerization was continued at these conditions for 48 hours, during which the system was homogeneous and clear. At the end of the polymerization, carbon dioxide was vented slowly
10 to leave the polymer in the cell. The polymer was dissolved with Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give a very tacky
15 material. The polymer was extracted with acetone overnight to remove any possible styrene homopolymer.

Characterizations: ¹H NMR and FTIR spectra were indicative of a random or statistical copolymer. All the peaks of FOA were shifted upfield by ca. 0.4
20 ppm. Also the peak of the methylene proton adjacent to the perfluoroalkyl chain was broadened. IR spectrum showed one carbonyl resonance at 1758 cm⁻¹ and peaks appeared in the region between 3000 to 3100 cm⁻¹ due to the stretching vibration of C-H on the phenyl ring of
25 the styrene repeating unit.

EXAMPLE 17

Copolymerization of FOA with Ethylene in CO₂

FOA (4.0 g, 6.6 mmol) and AIBN (50 mg, 0.30 mmol) were put into the high pressure cell. Ethylene
30 (0.46 g, 16.4 mmol) was transferred from a small bomb into the reaction cell. CO₂ was added, and the temperature was raised to 60°C and the total pressure was 5000 psi. The polymerization was allowed to proceed for ca. 48 hours. During this time period, the
35 system remained homogeneous and clear. After venting CO₂, the product was dissolved with Freon-113 and

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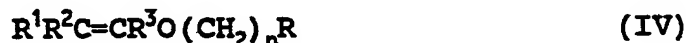
precipitated into large excess of methanol to give 2.9 g of viscous polymer (yield: 65%). The copolymer was extracted with boiling toluene for two hours to remove any polyethylene homopolymer.

5 Characterization: The copolymer was insoluble in acetone, toluene, THF, chloroform and DMF. It was soluble in Freon-113. ¹H NMR spectrum showed a new peak appearing at ca. 1.5 ppm, which is presumably due to the protons of the ethylene repeat unit. FTIR shows
10 similar pattern to PFOA homopolymer. The resonance of ethylene repeat unit may be buried by the resonance of the backbone of FOA. Intrinsic viscosity was measured to be 0.14 dL/g in Freon-113 at 30°C.

EXAMPLE 18

15 Cationic Polymerization of Vinyl Ethers in CO₂

Vinyl ethers with a fluoroalkyl group according to Formula (IV):



wherein:

20 n is 0, 1, or 2;

R¹, R², and R³ are each independently hydrogen or fluorine; and

R is perfluorinated aliphatic or perfluorinated aromatic group,

25 for example, CH₂=CH-OCH₂CH₂N(n-C₃H₇)SO₂C₈F₁₇ or CH₂=CH-OCH₂C₈F₁₇, are polymerized with an initiator such as boron trifluoroetherate, hydrogen iodine/iodine, and hydrogen iodine/zinc iodine in liquid and supercritical carbon dioxide using the procedure of Example 4 above.

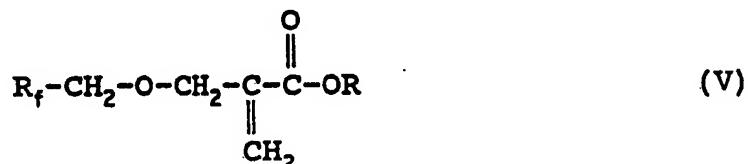
30 It has previously been known that these monomers could be solvent polymerized in Freon. See W. Choi et al., *Polymer J.* 20, 201 (1988). Thus, this example indicates that the ability of a monomer to undergo solution polymerization in Freon-113 is a good

indicator that the monomer can be polymerized in liquid or supercritical carbon dioxide.

EXAMPLE 19

Polymerization of 1,1-Disubstituted Monomers

1,1-disubstituted monomers according to Formula (V):



wherein R is C1-C4 alkyl (e.g., ethyl) and R_f is (CF₂)_nF wherein n is 1-10, (e.g., CF₃, (CF₂)₂F, (CF₂)₇F, or (CF₂)₁₀F), are polymerized in liquid or supercritical carbon dioxide under conditions using the procedure of Example 4 above.

EXAMPLE 20

Polymerization with Chain Transfer Agents

Functional fluoropolymers are produced in liquid or supercritical carbon dioxide by polymerizing a fluoromonomer such as FOA in carbon dioxide in the presence of a chain transfer agent such as substituted allylic sulfides. This results in fluoropolymers capped with a carboxy, hydroxy, trialkylsilyl, or amino groups.

EXAMPLE 21

Polymerization of Block Fluoropolymers

Block fluoropolymers are produced in liquid or supercritical carbon dioxide using the procedure of Example 4 above, using pseudo-living free radical polymerization routes. For example, FOA is polymerized in carbon dioxide with nitroxides similar to that disclosed in U.S. Patent No. 4,581,429 or with oxygen-

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centered radical species generated from hyponitrite, arenediazoate, or cyanate anions by reaction with electron acceptors such as arenediazonium ions or activated alkyl halides with sequential monomer additions, similar to Druliner, J.D., *Macromolecules* 1991, 24, 6079.

EXAMPLE 22

Poly(perfluoroalkyl ether) Polymerization

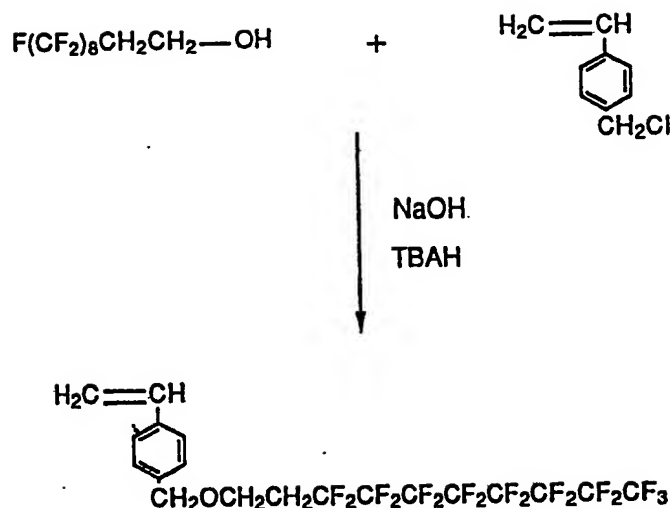
Poly(perfluoroalkyl ether)s are made in liquid or supercritical carbon dioxide using the procedure of Example 4 above. For example, perfluoropropylene oxide is polymerized using initiators derived from alkali metal fluorides and an acid fluoride such as $\text{CF}_3\text{CO-F}$ in carbon dioxide to yield viscous oils.

EXAMPLE 23

Preparation of Monomers

Styrene (Aldrich), methyl methacrylate (MMA) (Aldrich), acrylic acid (AA) (Aldrich) were purified by running through an alumina column and deoxygenated before polymerization. N-Octyl acrylate (OA), octadecyl methacrylate (ODMA) and all the perfluoroalkyl acrylates described above in Example 1 were purified in a similar fashion. Vinylidene fluoride (VF_2) (Aldrich, 99+%) and pentafluorostyrene (5FSt) (PCR Inc.) were used as received. The styrene-based monomer carrying a fluorocarbon segment, p-perfluoroalkylethyleneoxymethyl styrene (STF), was prepared by a phase-transfer-catalyzed etherification of fluorocarbon-substituted alcohol with p-(chloromethyl) styrene:

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EXAMPLE 24

Homopolymerization of Fluorostyrene Monomer
p-perfluoroalkylethyleneoxymethyl Styrene (STF)

A typical example of a homopolymerization in supercritical CO₂ was conducted as follows. STF (1.0 g, 1.72 mmol) and AIBN (30 mg, recrystallized twice from methanol) were put into a 10-mL high pressure view cell containing a micromagnetic stir bar. The reaction cell was purged with argon for ca. 10 minutes, and then filled with CO₂ to less than 68 bar. The cell was heated to 60°C and the pressure was increased to 345 bar by the addition of more CO₂. The polymerization was continued at these conditions for 3 days, during which time the system remained homogeneous and optically transparent. At the end of the polymerization, the cell was cooled to room temperature and CO₂ was vented resulting in the precipitation of the polymer. The unreacted monomer was extracted with dichloromethane. The polymer was dried to constant weight and characterized (65% yield).

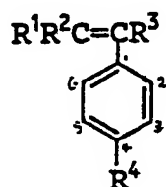
The other monomers (VF₂, 5FSt, styrene, MMA, AA) were all homopolymerized in supercritical carbon dioxide according to a procedure similar to that above;

however, these polymers precipitated during the course of the reaction in CO₂ under the conditions described.

EXAMPLE 25

Homopolymerization of Fluorostyrene Monomer

5 Fluorostyrene monomers according to Formula (VI):



(VI)

wherein:

- 10 R¹ and R² are each independently hydrogen, fluorine, or methyl;
 R³ is hydrogen, fluorine, methyl or perfluoromethyl;
 R⁴ is hydrogen, fluorine, or C1-C12
 15 perfluorinated aliphatic group; and
 the 2, 3, 5, and 6 positions of the aromatic styrene ring are each independently hydrogen or fluorine, are polymerized with an initiator such as AIBN in liquid and supercritical carbon dioxide using
 20 the concentrations and procedure of Example 24 above.

EXAMPLE 26

Copolymerization of Fluorinated Monomer (Fluoroacrylate MeFOSEA) with Non-Fluorinated Comonomer (OA)

- A copolymerization of the fluorinated
 25 monomers with non-fluorinated monomers in supercritical CO₂ was conducted as follows. 2-(N-Methylperfluoro-octanesulfonamido) ethyl acrylate (MeFOSEA, 1.3 g, 2.12 mmol), OA (0.70 g, 3.80 mmol) and AIBN (30 mg, 0.18 mmol) were put into the 10-mL high pressure view cell.
 30 Following the procedure as described above in Example 24, the copolymerization was continued at 60°C and 345 bar for 24 hours. The system was homogeneous during the entire course of the polymerization. After venting

the CO₂, the copolymer was redissolved in Freon-113 and precipitated into large excess of methanol. The polymer was filtered and washed with methanol several times and dried in vacuum overnight to give 1.35 g of copolymer (68% yield).

The other non-fluorinated monomers are also copolymerized in a similar fashion.

EXAMPLE 27

Copolymerization of Fluorinated Monomer (Fluoroacrylate FOA) With Fluorinated Comonomer (Vinylidene Fluoride)

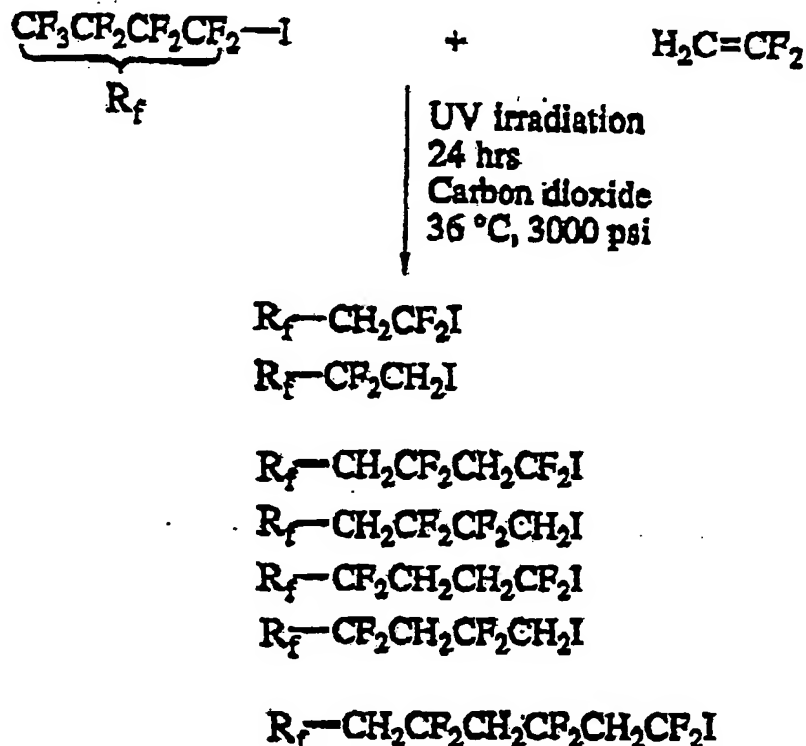
The 10-mL high pressure cell was loaded with 1,1-dihydroperfluorooctyl acrylate (FOA, 3.0 g, 6.6 mmol) and AIBN (50 mg, 0.30 mmol). After purging with argon thoroughly, the cell was connected to a VF₂ cylinder, 3.02 of VF₂ (47.2 mmol) was transferred into the cell by cooling down the cell in a dry ice/isopropanol bath. After warming the cell to room temperature, carbon dioxide was filled to ca. 68 bar. The heating of the cell was continued and more CO₂ was added until the cell reached 60°C and 345 bar. The polymerization was continued at these conditions for ca. 50 hours during which the system was homogeneous during the entire course of the reaction. The copolymer was obtained according to the same work-up procedure.

EXAMPLE 28

Polymerization of 1,1-difluoroethylene (VF₂)

A low molecular weight polymer or oligomer was made in carbon dioxide by polymerizing 1,1-difluoroethylene (VF₂) in the presence of a perfluor alkyl iodide. 1.0 g of C₄F₉I and 2.0 g of VF₂ was transferred into a 10-mL stainless steel cell fitted with sapphire windows. The cell was heated to 36°C and filled to 3000 psi with carbon dioxide. The reaction was homogeneous (optically transparent and

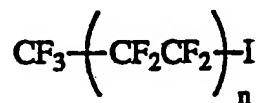
colorless). The cell was irradiated with an ultraviolet lamp for 24 hours, during which time the reaction remained homogeneous and turned color from colorless to light purple or pink.



5 The product distribution was determined by gas chromatography-mass spectrometry to include the various products listed above with the various regioisomers as shown.

EXAMPLE 29

10 A low molecular weight polymer or oligomer is made in carbon dioxide by polymerizing tetrafluoroethylene (TFE) using the concentrations and procedures of Example 28 above, but in the presence of a chain transfer agent such as trifluoromethyl iodide
15 or IF to yield:



or



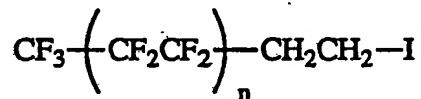
under homogeneous conditions in a stainless steel or Hastalloy reactor/view cell.

EXAMPLE 30

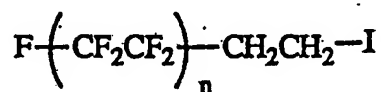
Following the procedure set forth in Example 28 and 29 above, fluoroolefins, such as tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), perfluoro-2,2-dimethyl-1,3-dioxole or mixtures of these monomers, or with the addition of ethylene monomer, are polymerized under homogeneous conditions in carbon dioxide.

EXAMPLE 31

Low molecular weight polymers or oligomers are made in carbon dioxide using a process essentially as described in Examples 28, 29 and 30 above, but the reaction product is endcapped with ethylene to yield:



or



EXAMPLE 32

A dimer, oligomer or low molecular weight polymer of CTFE, HFP, TFE, or VF₂ is obtained by following the procedures of Example 28 above, except that the fluoroolefin or mixtures of the fluoroolefins are treated with I₂ or another Lewis acid (such as FeCl₃) in carbon dioxide to form a product soluble in carbon dioxide. Halogenated chain transfer agents or telogens such as Cl₃CBr, CFCl₃, CFCF₃, CCl₄, Br-CFCl-CF₂-Br are optionally added. The reactions are optionally facilitated by UV irradiation or added peroxide.

EXAMPLE 33

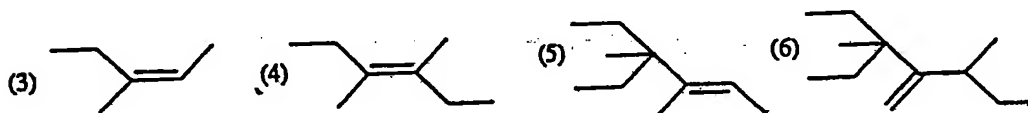
Terpolymerization of Fluoroolefin Monomers

A fluoropolymer is made by terpolymerizing TFE, CTFE, and ethylen in carbon dioxide using a peroxide initiator and a chain transfer agent such as freon-11 and the following ratios of TFE/CTFE/Ethylene: 20/45/35; 10/55/35; and 30/30/40.

EXAMPLE 34

Polymerization of Fluoroolefin TFE

An oligomer or low molecular weight polymer of TFE is made in carbon dioxide by treating TFE with a nucleophile in carbon dioxide oxide to form a carbon dioxide-soluble product, such as trimer, tetramer, pentamer and hexamer.



EXAMPLE 35

Polymerization of Fluoroolefin HFP

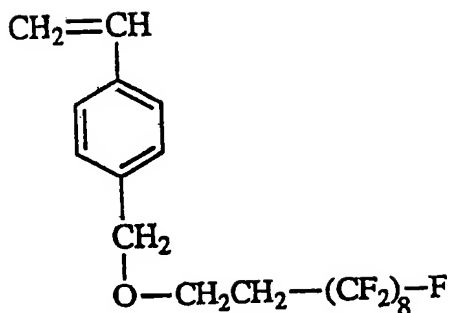
An oligomer or low molecular weight polymer of hexafluoropropylene (HFP) is obtained by treating HFP with a nucleophile such as CsF in carbon dioxide to form a soluble product in carbon dioxide.

EXAMPLE 36

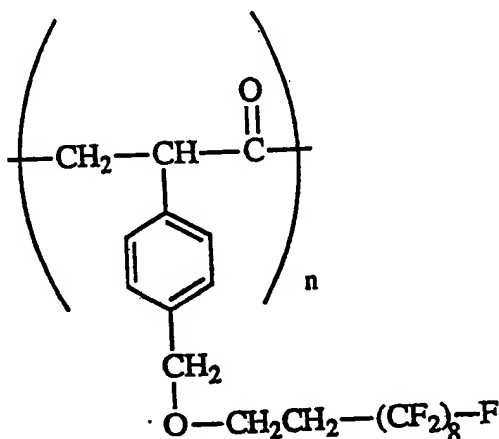
Polymerization of FluorostyreneMonomer STF Using a Palladium Catalyst

A polymer is made in carbon dioxide under the homogeneous conditions by copolymerizing a fluorinated monomer, such as:

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with carbon monoxide using a palladium catalyst (for concentrations, see, e.g., M. Brookhart et al., J. Am. Chem. Soc. 114, pg. 5894 (1992)) to yield:



EXAMPLE 37

5 Polymerization Using a Cosolvent

A polymerization is carried out in essentially the same manner as described above, except that a cosolvent is added to carbon dioxide, such as less than about 5% by weight diglyme, to form a product
10 soluble in carbon dioxide.

EXAMPLE 38

Isolation of Polymer

A process is carried out in essentially the same manner as described in Examples 23-37 above, except that the product is isolated either all at once
15 by continuous reduction of pressure (venting) or is

isolated in fractions by controlled release or stepwise reduction of pressure and subsequent collection and separation of the product.

EXAMPLE 39

5 Solubility of Fluoroolefin Polymer TFE

A low molecular weight polymer or oligomer of tetrafluoroethylene (TFE) with the structure:



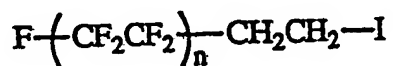
where $n = 1-5$, was completely dissolved in carbon dioxide at 5000 psi and 60°C.

10

EXAMPLE 40

Solubility of Endcapped Fluoroolefin Polymer TFE

A low molecular weight polymer or oligomer of TFE which was endcapped with ethylene, having the structure:



15 where $n = 1-5$, was dissolved in carbon dioxide at 2000 psi and 60°C.

EXAMPLE 41

Solubility of Fluoroolefin Polymer CTFE

20 A low molecular weight polymer or oligomer of chlorotrifluoroethylene (CTFE) with the structure:

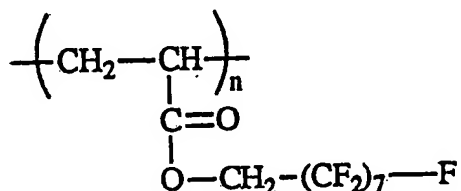


was dissolved in carbon dioxide over a wide range of pressures and weight fractions. The phase diagram at 40°C as shown in Figure 1 was determined.

EXAMPLE 42

5 Solubility of Fluoroacrylate Polymer FOA

A high molecular weight polymer of (1,1-dihydroperfluorooctyl) acrylate with the structure:

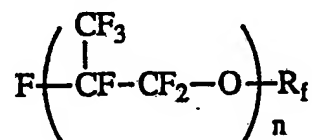


10 was dissolved in carbon dioxide over a wide range of pressures and weight fractions. The phase diagram at 60°C as shown in Figure 2 was determined.

EXAMPLE 43

Solubility of Fluoroalkylene Oxide Polymer

A low molecular weight polymer or oligomer of hexafluoropropylene oxide (Krytox) with the structure:



15 was dissolved in carbon dioxide at 5000 psi and 60°C.

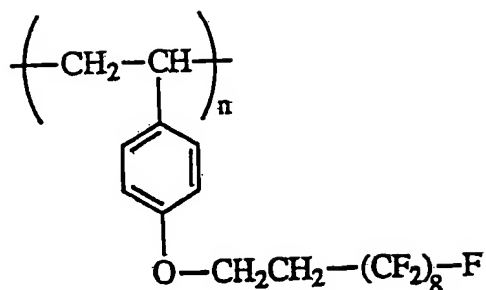
EXAMPLE 44

Solubility of Fluorostyrene Polymer

A high molecular weight polymer of a fluoroalkylsubstituted styren monomer with the structure:

20

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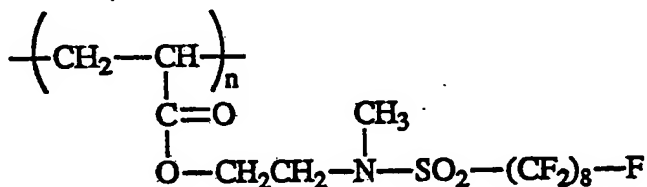


was dissolved in carbon dioxide at 5000 psi and 60°C.

EXAMPLE 45

Solubility of Fluoroacrylate Polymer MeFOSEA

A high molecular weight polymer with the structure:

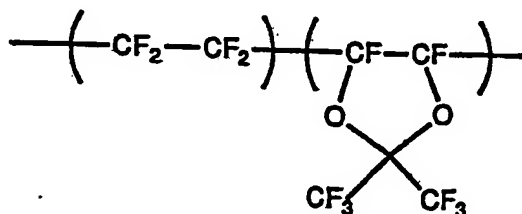


was dissolved in carbon dioxide at 5000 psi and 60°C.

EXAMPLE 46

Solubility of Fluoroolefin-Teflon Copolymer

A high molecular weight statistical copolymer of TFE and perfluoro-2,2-dimethyl-1,3-dioxole (Teflon AF 1600) having the following structure:



was heated to 80°C and pressurized to 6000 psi with carbon dioxide. At these conditions two liquid phases formed — a polymer rich phase and a carbon dioxide rich phase. Upon venting, the carbon dioxide-rich phase

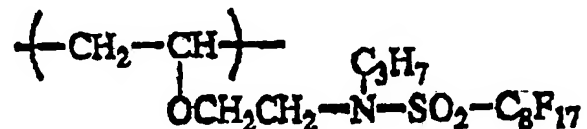
-41-

turned cloudy indicating that some of the polymer dissolved in carbon dioxide.

EXAMPLE 47

Solubility of Fluorinated Vinyl Ether Polymer

5 A high molecular weight polymer with the structure:



was dissolved in carbon dioxide at 3490 psi at 60°C. The polymer also dissolves in freon-113, but is insoluble in common organic solvents such as THF, dichloromethane, and chloroform.

10

The foregoing examples are illustrative of the present invention, and are not to be taken as restrictive thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

15

THAT WHICH IS CLAIMED IS:

1. A process for making a fluoropolymer, comprising:

5 solubilizing a fluoromonomer selected from the group consisting of fluoroacrylate monomers, fluoroolefin monomers, fluorostyrene monomers, fluorinated vinyl ether monomers, and fluoroalkylene oxide monomers in a solvent, the solvent comprising carbon dioxide fluid; and then

10 polymerizing the fluoromonomer in said solvent to produce said fluoropolymer.

2. A process according to claim 1, wherein said carbon dioxide fluid is liquid carbon dioxide.

3. A process according to claim 1, wherein said carbon dioxide fluid is supercritical carbon dioxide.

4. A process according to claim 1, further comprising the step of separating said fluoropolymer from said carbon dioxide and collecting said fluoropolymer.

5. A process according to claim 4, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

6. A process according to claim 1, further comprising:

solubilizing a comonomer in said carbon dioxide fluid,

5 and wherein said polymerizing step comprises copolymerizing said fluoromonomer with said comonomer.

7. A process according to claim 1, wherein said polymerizing step is carried out in the presence of an initiator.

8. A process according to claim 1, wherein said solvent further comprises a cosolvent.

9. A process according to claim 1, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

10. A process for making a fluoroacrylate polymer, comprising:

solubilizing a fluoroacrylate monomer in a solvent, the solvent comprising carbon dioxide fluid;
5 and then

polymerizing the fluoroacrylate monomer in said solvent to produce said fluoroacrylate polymer.

11. A process according to claim 10, wherein said carbon dioxide fluid is liquid carbon dioxide.

12. A process according to claim 10, wherein said carbon dioxide fluid is supercritical carbon dioxide.

13. A process according to claim 10, further comprising the step of separating said fluoropolymer from said carbon dioxide and collecting said fluoropolymer.

14. A process according to claim 13, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

15. A process according to claim 10, further comprising:

solubilizing a comonomer in said carbon dioxide fluid,

5 and wherein said polymerizing step comprises copolymerizing said fluoromonomer with said comonomer.

16. A process according to claim 10, wherein said polymerizing step is carried out in the presence of an initiator.

17. A process according to claim 10, wherein said solvent further comprises a cosolvent.

18. A process according to claim 10, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

19. A process for making a fluoroacrylate polymer, comprising:

5 solubilizing a fluoroacrylate monomer in a solvent, the solvent comprising carbon dioxide fluid wherein said fluoroacrylate monomer comprises a monomer of formula (I):



wherein:

10 n is 1 or 2;
R¹ is hydrogen or methyl; and
R² is a perfluorinated aliphatic or perfluorinated aromatic group; and then
polymerizing the fluoroacrylate monomer in said solvent to produce said fluoroacrylate polymer.

20. A process according to claim 19, wherein R^2 is a C1 to C8 perfluoroalkyl or $-CH_2NR^3SO_2R^4$, wherein R^3 is C1-C2 alkyl and R^4 is C1 to C8 perfluoroalkyl.

21. A process according to claim 19, wherein said fluoroacrylate monomer is selected from the group consisting of:

5 2-(N-ethylperfluorooctanesulfonamido) ethyl
acrylate;

 2-(N-ethylperfluorooctanesulfonamido) ethyl
methacrylate;

 2-(N-methylperfluorooctanesulfonamido) ethyl
acrylate;

10 2-(N-methylperfluorooctanesulfonamido) ethyl
methacrylate;

 1,1-Dihydroperfluorooctyl acrylate; and
 1,1-Dihydroperfluorooctyl methacrylate.

22. A process according to claim 19, wherein said carbon dioxide fluid is liquid carbon dioxide.

23. A process according to claim 19, wherein said carbon dioxide fluid is supercritical carbon dioxide.

24. A process according to claim 19, further comprising the step of separating said fluoropolymer from said carbon dioxide and collecting said fluoropolymer.

25. A process according to claim 24, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

26. A process according to claim 19, further comprising:

solubilizing a comonomer in said carbon dioxide fluid,

5 and wherein said polymerizing step comprises copolymerizing said fluoromonomer with said comonomer.

27. A process according to claim 19, wherein said polymerizing step is carried out in the presence of an initiator.

28. A process according to claim 19, wherein said solvent further comprises a cosolvent.

29. A process according to claim 19, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

30. A process for making a fluoroalkylene oxide polymer, comprising:

solubilizing a fluoroalkylene oxide monomer in a solvent comprising carbon dioxide fluid; and then

5 polymerizing the fluoroalkylene oxide monomer in said solvent to produce said fluoroalkylene oxide polymer.

31. A process according to Claim 30 wherein said fluoroalkylene oxide monomer is selected from the group consisting of perfluoropropylene oxide and perfluorocyclohexene oxide.

32. A process according to claim 30, wherein said carbon dioxide fluid is liquid carbon dioxide.

33. A process according to claim 30, wherein said carbon dioxide fluid is supercritical carbon dioxide.

34. A process according to claim 30, further comprising the step of separating said fluoroalkylene oxide polymer from said carbon dioxide and collecting said fluoroalkylene oxide polymer.

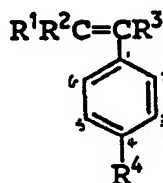
35. A process according to claim 35, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

36. A process for making a fluorostyrene polymer, comprising:

solubilizing a fluorostyrene monomer in a solvent comprising carbon dioxide fluid; and then

5 polymerizing the fluorostyrene monomer in said solvent to produce said fluorostyrene polymer.

37. A process according to Claim 36, wherein said fluorostyrene monomer comprises a monomer of Formula (VI):



(VI)

wherein:

R¹ and R² are each independently hydrogen, fluorine, or methyl;

10 R³ is hydrogen, fluorine, methyl or perfluoromethyl;

R⁴ is hydrogen, fluorine, or C1-C12 perfluorinated aliphatic group; and

15 wherein the 2, 3, 5, and 6 positions of the aromatic styrene ring are each independently hydrogen or fluorine.

38. A process according to claim 36, wherein said carbon dioxide fluid is liquid carbon dioxide.

39. A process according to claim 36, wherein said carbon dioxide fluid is supercritical carbon dioxide.

40. A process according to claim 36, further comprising the step of separating said fluorostyrene polymer from said carbon dioxide and collecting said fluorostyrene polymer.

41. A process according to claim 40, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

42. A process for making a fluorinated vinyl ether polymer comprising:

solubilizing a fluorinated vinyl ether monomer in a solvent comprising carbon dioxide fluid;
and then

polymerizing the fluorinated vinyl ether monomer in said solvent to produce said fluorinated vinyl ether polymer.

43. A process according to Claim 42, wherein said fluorinated vinyl ether monomer comprises a monomer of Formula (IV):



wherein:

n is 0, 1 or 2;

R¹, R², and R³ are each independently hydrogen or fluorine; and

R is perfluorinated aliphatic or perfluorinated aromatic group.

44. A process according to claim 42, wherein said carbon dioxide fluid is liquid carbon dioxide.

45. A process according to claim 42, wherein said carbon dioxide fluid is supercritical carbon dioxide.

46. A process according to claim 42, further comprising the step of separating said fluorinated vinyl ether polymer from said carbon dioxide and collecting said fluorinated vinyl ether polymer.

47. A process according to claim 46, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

48. A process for making a fluoroolefin polymer comprising:

solubilizing a fluoroolefin monomer in a solvent comprising carbon dioxide fluid; and then

5 polymerizing the fluoroolefin monomer in said solvent to produce said fluoroolefin polymer.

49. A process according to Claim 48 wherein said fluoroolefin monomer is selected from the group consisting of difluoroethylene, tetrafluoroethylene, hexafluoropropylene, chlorotrifluoroethylene,
5 perfluoro-2,2-dimethyl-1,3-dioxole and mixtures thereof.

50. A process according to claim 48, wherein said carbon dioxide fluid is liquid carbon dioxide.

51. A process according to claim 48, wherein said carbon dioxide fluid is supercritical carbon dioxide.

52. A process according to claim 48, further comprising the step of separating said fluoroolefin polymer from said carbon dioxide and collecting said fluoroolefin polymer.

53. A process according to claim 52, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

AMENDED CLAIMS

[received by the International Bureau on 13 September 1993 (13.09.93) ;
original claims 1-53 replaced by amended claims 1-26 (6 pages)]

1. A process for making a fluoropolymer,
comprising:

solubilizing a fluoromonomer selected from the
group consisting of fluoroacrylate monomers,
fluoroolefin monomers, fluorostyrene monomers,
fluorinated vinyl ether monomers, and fluoroalkylene
oxide monomers in a solvent, the solvent comprising
carbon dioxide fluid; and then

polymerizing the fluoromonomer in said solvent to
produce said fluoropolymer;

wherein said polymerizing step is a solution
polymerization step.

2. A process according to claim 1, wherein said
polymerizing step is carried out in the presence of a
chain transfer agent.

3. A process for making a fluoroacrylate polymer,
comprising:

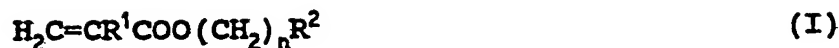
solubilizing a fluoroacrylate monomer in a
solvent, the solvent comprising carbon dioxide fluid;
and then

polymerizing the fluoroacrylate monomer in said
solvent to produce said fluoroacrylate polymer.

4. A process according to claim 3, wherein said
polymerizing step is carried out in the presence of a
chain transfer agent.

5. A process for making a fluoroacrylate polymer,
comprising:

solubilizing a fluoroacrylate monomer in a
solvent, the solvent comprising carbon dioxide fluid
wherein said fluoroacrylate monomer comprises a monomer
of formula (I):



Wherein:

n is 1 or 2;

R¹ is hydrogen or methyl; and

R² is a perfluorinated aliphatic or perfluorinated aromatic group; and then

polymerizing the fluoroacrylate monomer in said solvent to produce said fluoroacrylate polymer.

6. A process according to claim 5, wherein R² is a C1 to C8 perfluoroalkyl or -CH₂NR³SO₂R⁴, wherein R³ is C1-C2 alkyl and R⁴ is C1 to C8 perfluoroalkyl.

7. A process according to claim 5, wherein said fluoroacrylate monomer is selected from the group consisting of:

2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate;

2-(N-ethylperflooctanesulfonamido) ethyl methacrylate;

2-(N-methylperfluorooctanesulfonamido) ethyl acrylate;

2-(N-methylperflooctanesulfonamido) ethyl methacrylate;

1,1-Dihydroperfluorooctyl acrylate; and

1,1-Dihydroperfluorooctyl methacrylate.

8. A process according to claim 5, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

9. A process for making a fluoroalkylene oxide polymer, comprising:

solubilizing a fluoroalkylene oxide monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluoroalkylene oxide monomer in said solvent to produce said fluoroalkylene oxide polymer.

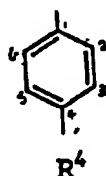
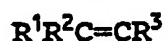
10. A process according to Claim 9 wherein said fluoroalkylene oxide monomer is selected from the group consisting of perfluoropropylene oxide and perfluorocyclohexene oxide.

11. A process for making a fluorostyrene polymer, comprising:

solubilizing a fluorostyrene monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluorostyrene monomer in said solvent to produce said fluorostyrene polymer.

12. A process according to Claim 11, wherein said fluorostyrene monomer comprises a monomer of Formula (VI):



(VI)

wherein:

R^1 and R^2 are each independently hydrogen, fluorine, or methyl;

R^3 is hydrogen, fluorine, methyl or perfluoromethyl;

R^4 is hydrogen, fluorine, or C1-C12 perfluorinated aliphatic group; and

wherein the 2, 3, 5, and 6 positions of the aromatic styrene ring are each independently hydrogen or fluorine.

13. A process for making a fluorinated vinyl ether polymer comprising:

solubilizing a fluorinated vinyl ether monomer in a solvent comprising carbon dioxide fluid; and then polymerizing the fluorinated vinyl ether monomer in said solvent to produce said fluorinated vinyl ether polymer.

14. A process according to Claim 13, wherein said fluorinated vinyl ether monomer comprises a monomer of Formula (IV):



wherein:

n is 0, 1 or 2;

R^1 , R^2 , and R^3 are each independently hydrogen or fluorine; and

R is perfluorinated aliphatic or perfluorinated aromatic group.

15. A process for making a fluoroolefin polymer comprising:

solubilizing a fluoroolefin monomer in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluoroolefin monomer in said solvent to produce said fluoroolefin polymer;

wherein said polymerizing step is a solution polymerization step.

16. A process according to Claim 15, wherein said fluoroolefin monomer is selected from the group consisting of difluoromethane, tetrafluoroethylene, hexafluoropropylene, chlorotrifluoroethylene,

perfluoro-2,2-dimethyl-1,3-dioxole and mixtures thereof.

17. A process according to claim 15, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

18. A process according to claim 15, wherein said fluoroolefin polymer is an amorphous tetrafluoroethylene copolymer.

19. A process according to claim 15, wherein said fluoroolefin polymer is an amorphous fluoroolefin polymer which is a fluorocarbon elastomer.

20. A process according to claim 1, 3, 5, 9, 11, 13, or 15, wherein said carbon dioxide fluid is liquid carbon dioxide.

21. A process according to claim 1, 3, 5, 9, 11, 13, or 15, wherein said carbon dioxide fluid is supercritical carbon dioxide.

22. A process according to claim 1, 3, 5, 9, 11, 13, or 15, further comprising the step of separating said polymer from said carbon dioxide and collecting said polymer.

23. A process according to claim 19, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

24. A process according to claim 1, 3, 5, 9, 11, 13, or 15, further comprising:

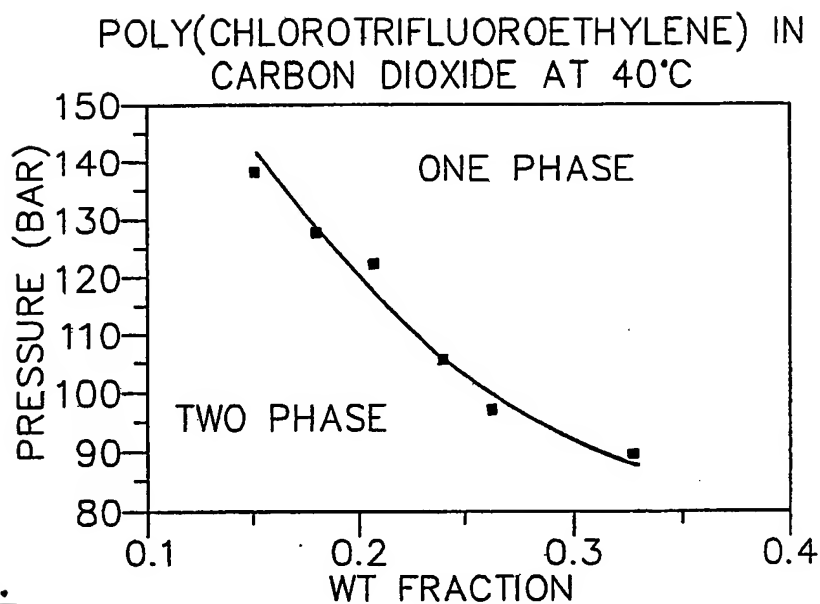
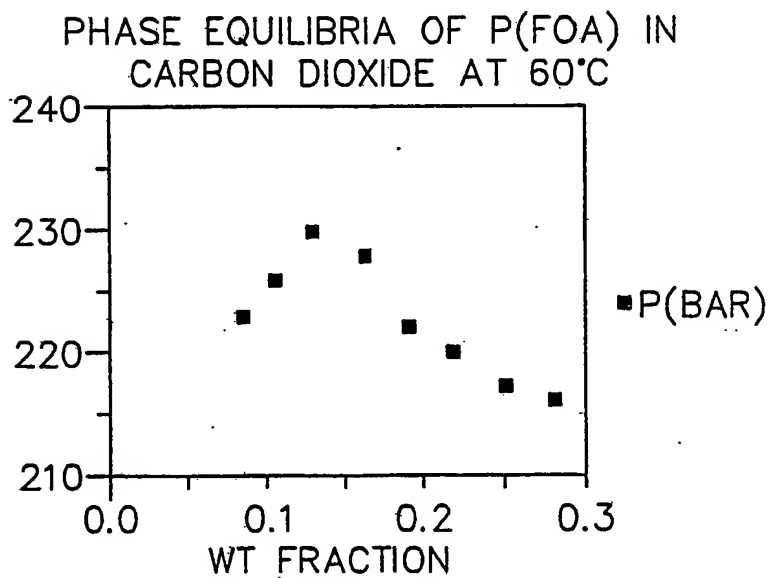
solubilizing a comonomer in said carbon dioxide fluid,

and wherein said polymerizing step comprises copolymerizing said fluoromonomer with said comonomer.

25. A process according to claim 1, 3, 5, 9, 11, 13, or 15, wherein said polymerizing step is carried out in the presence of an initiator.

26. A process according to claim 1, 3, 5, 9, 11, 13, or 15, wherein said solvent further comprises a cosolvent.

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FIG. 1.FIG. 2.

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)* According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08F14/18; C08F20/22; C08F2/06		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB,A,1 172 713 (SUMITOMO CHEM. CO. LTD.) 3 December 1969 see claim 1 see page 2, line 58 - page 2, line 76 see page 3, line 13 - page 3, line 21 ---	1-4, 48-50
A	EP,A,0 239 035 (BASF) 30 September 1987 ---	
A	EP,A,0 301 532 (B.F.GOODRICH CO.) 1 February 1989 -----	
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>⁹ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search <div style="text-align: center; font-size: 1.2em;">17 JUNE 1993</div>		Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">3. 07. 93</div>
International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>		Signature of Authorized officer <div style="text-align: center; font-weight: bold;">CAUWENBERG C.L.</div>

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9301626
SA 71621

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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17/06/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US-A- 3522228	28-07-70
EP-A-0239035	30-09-87	DE-A- 3609829	24-09-87
		JP-A- 62232413	12-10-87
		US-A- 4748220	31-05-88
EP-A-0301532	01-02-89	AU-A- 2021288	09-02-89
		JP-A- 1163203	27-06-89

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